

# Oxidation Kinetics and Soot Formation

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## Abstracts and Figures

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SHOCK TUBE STUDY OF THE FUEL MOLECULAR  
STRUCTURE EFFECTS ON THE CHEMICAL KINETIC MECHANISMS  
FOR SOOT FORMATION

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33774

P-5

OBJECTIVE:

The objective of this research effort is to investigate the gas-phase mechanisms which lead to soot formation in the combustion of complex hydrocarbon fuels.

BACKGROUND:

Aromatic species are believed to be closely related to mechanisms for soot formation in the combustion of hydrocarbon fuels. Recent investigations have produced evidence that the fragmentation products of parent aromatic fuels initiate the reaction sequence leading to the formation of embryonic soot precursors.<sup>1-4</sup> It is likely that the key fragmentation products for parent aromatics such as toluene and benzene include resonance-stabilized free radicals similar to the allyl or butadienyl radicals, and possibly the phenyl and benzyl radicals as well. To test this concept and to elucidate which decomposition pathways lead to soot initiation, we are examining the comparative sooting behavior of toluene and three potential toluene decomposition products: benzene, allene, and 1,3-butadiene.

APPROACH:

The fuel decomposition is studied under pyrolytic and oxidative conditions behind incident shock waves, using various optical diagnostics to monitor particle appearance and the behavior of gas phase species. In particular, we are investigating: (1) improved quantification of UV/visible soot yield measurements using infrared attenuation and emission techniques; (2) spectral characteristics of gas-phase emission and absorption in the ultraviolet, visible, and infrared; and (3) a conceptual view of the chemical pathways for fuel decomposition and the gas-phase reactions leading to soot formation.

To address the first point, we have supplemented our existing attenuation diagnostics (389 nm He line, 633 nm HeNe laser line) with attenuation at 3.39  $\mu\text{m}$  (HeNe laser line) and absolute emission at 5  $\mu\text{m}$ . We have performed limited spectral survey experiments using two UV/visible monochromators and a fast-scanning infrared spectrometer.

The remainder of the research program is directed towards a systematic study of the comparative pyrolytic and oxidative sooting behavior of the sequence of resonance-stabilized hydrocarbons, toluene, benzene, butadiene, allene, and acetylene. Of these species, we selected benzene and allene for more detailed study. The principle observations include initial sooting rates, soot yields, and particle size parameters as functions of temperature; additional diagnostics include optical measurements of the kinetic behavior of hydrocarbon species where possible. We are using limited kinetic modeling computations to aid in optimizing test mixtures and interpreting results, and are attempting to construct a conceptual model of the soot initiation process.

## STATUS:

A typical set of optical data is shown in Fig. 1. As observed previously for toluene,<sup>4</sup> ratios of the 633 nm attenuation signal to ultraviolet and infrared measurements indicate that this diagnostic detects primarily soot particles after about 0.5-1 ms (particle time). At early times, the ultraviolet absorption data appear to reflect the behavior of molecular species formed in the initial stages of fuel decomposition. The visible emission exhibits a distinctly different kinetic behavior from that of soot, and may arise from large hydrocarbon species found at an intermediate stage of the soot initiation sequence. All of these signatures are remarkably similar to those previously observed in toluene pyrolysis under the same conditions.<sup>4</sup>

Sooting delay times, initial formation rates, and yields obtained from the 633 nm data are compared in Figs. 2-4. The general behavior is remarkably similar for all fuels tested. The soot formation rates and yields pass through maxima near 1800 K, the temperature at the maximum being lower for allene than for benzene and lower for benzene than for toluene. In contrast, the apparent sooting delay times continue to decrease with temperature even though the rate parameters obtained at later times show an inverse kinetic behavior. This indicates that, at early times, a small amount of absorption occurs at 633 nm due to intermediate hydrocarbons formed in the fuel decomposition, and these delay times do not necessarily reflect the initiation of soot particles.

In an attempt to more fully characterize the optical signatures of soot initiation, we have performed a series of spectral survey experiments for toluene pyrolysis at ~ 2000 K and ~ 600 torr. These measurements include spectrally and temporally resolved surveys of UV absorption (200-400 nm), visible emission (400-700 nm), and IR emission (2-5  $\mu$ m), and exhibit spectral and kinetic signatures due to soot and hydrocarbon intermediates. In addition, we have been able to deduce an absorption cross section for soot particles at 633 nm by ratioing visible attenuation measurements to absolute IR emission data. This value is in excellent agreement with that estimated earlier from ratios of UV and visible attenuation coupled with a Mie theory analysis,<sup>4</sup> but is significantly lower than values employed in previous soot yield measurements.<sup>5,6</sup>

The results obtained here contribute to a growing data base which lends itself to interpretation in terms of possible soot initiation mechanisms. It appears now that resonance-stabilized radicals formed by fragmentation of the parent ring compound are important participants in the molecular growth processes leading to soot formation. In order to attain substantial reaction rates, the growth sequence must be initiated by reactions of these radicals with fuel decomposition products which are present in large concentration, e.g.,  $C_2H_2$  or  $C_2H$ . In the remainder of the project, we plan to test this concept further in studies of benzene oxidation.

## References

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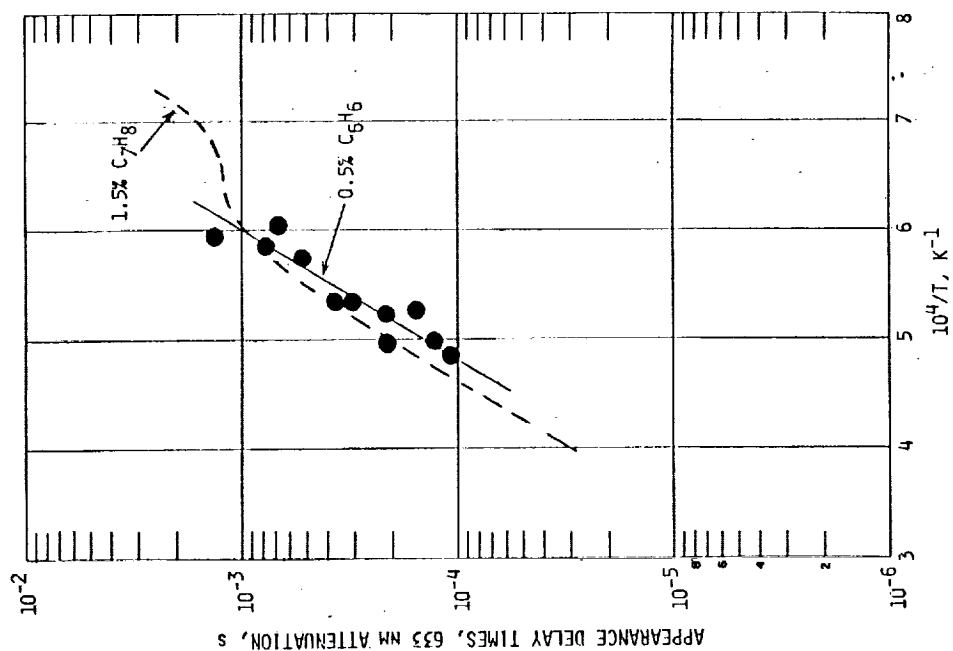


Fig. 2 Appearance delay times for 633 nm attenuation.

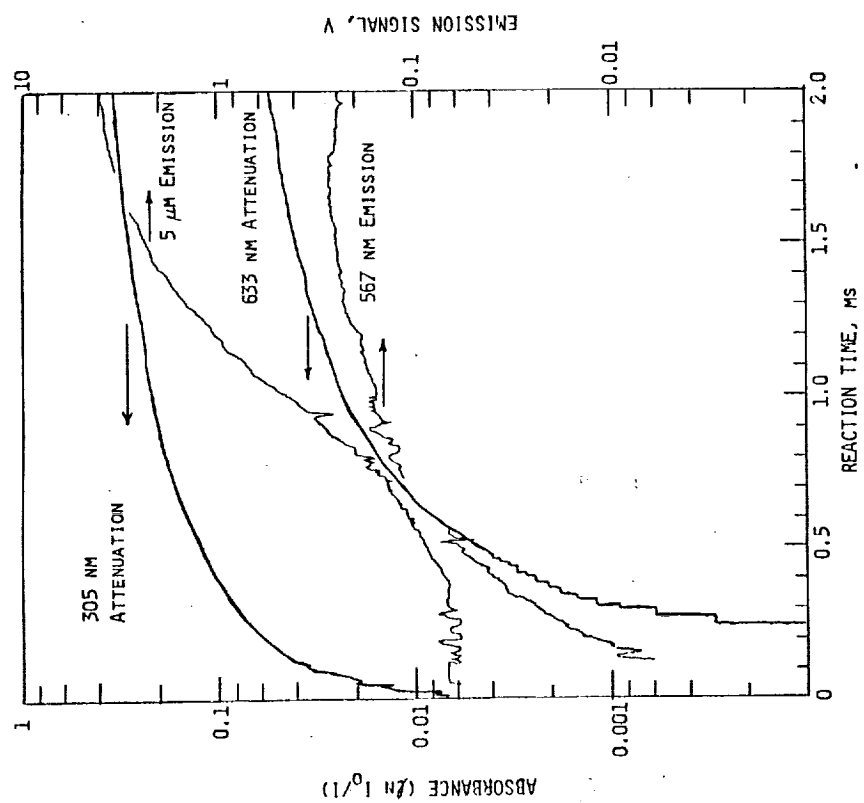


Fig. 1 Logarithmic plot of four optical signals vs. time for pyrolysis of 3.5%  $C_3H_4$ /96.5% Ar at 1725 K, 490 torr.



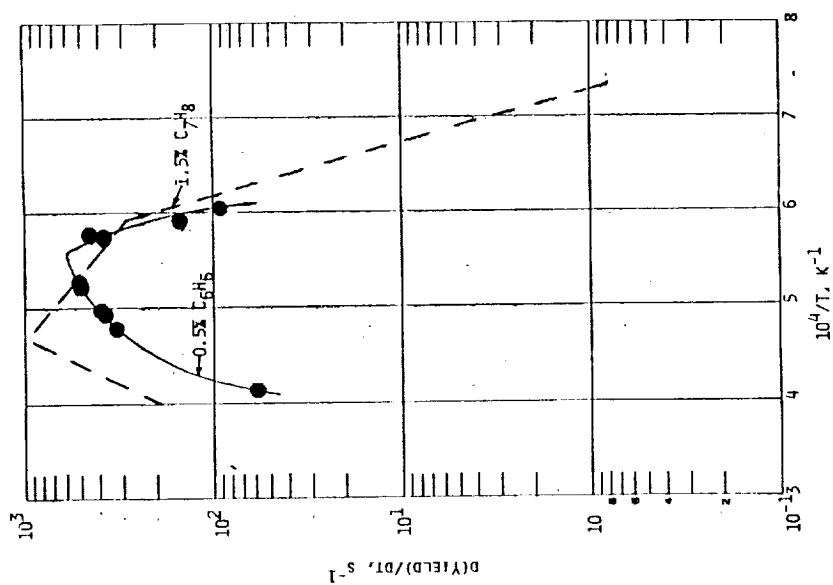


Fig. 3 Linearized soot appearance rates determined at 633 nm.

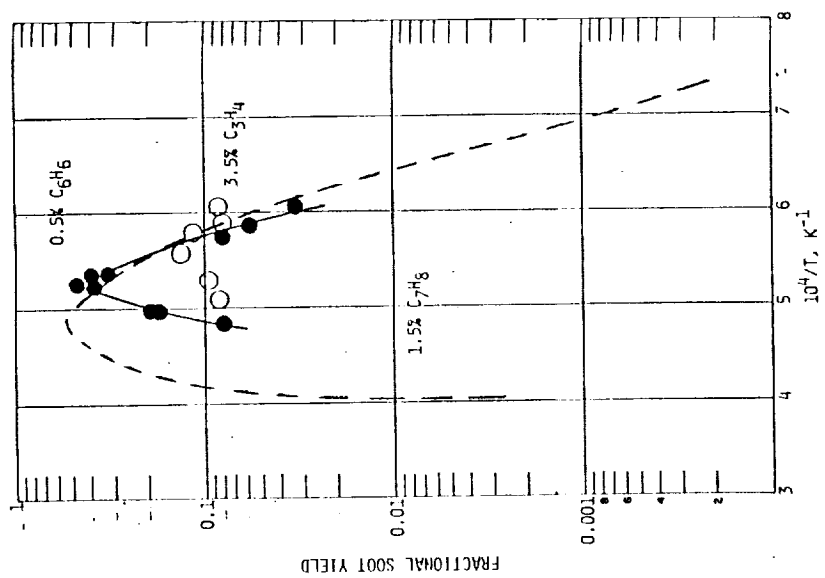


Fig. 4 Fractional soot yields at 1 ms determined from 633 nm attenuation.



SHOCK TUBE STUDY OF THE FUEL STRUCTURE EFFECTS ON THE CHEMICAL  
KINETIC MECHANISMS RESPONSIBLE FOR SOOT FORMATION

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OBJECTIVE:

The ultimate goal of our program is to develop a reliable model which is capable of predicting soot formation characteristics during combustion of hydrocarbon fuels.

BACKGROUND:

The formation of soot (or carbon particles) always accompanies the combustion of hydrocarbon fuels. Soot causes several undesirable effects such as increased combustor particulate emission and increased radiant heat transfer loads to interior walls in air-breathing combustors. Sooting is particularly severe with synthetic fuels because of their higher aromatic content. Although the recent oil crisis seems to be over, the development and future use of synthetic fuels are inevitable. There are many scientific and technological problems associated with these fuels; soot formation is certainly one of these challenging problems.

APPROACH:

Both experimental and theoretical studies have been conducted. The objective of the experimental part of the program is to establish quantitative relationships between the parameters of soot formation and experimental conditions, such as temperature, pressure, composition of the mixture and molecular structure of the fuel molecules. The experiments have involved pyrolysis and oxidation of a variety of fuels using state-of-the-art shock-tube, laser diagnostic and data processing techniques.

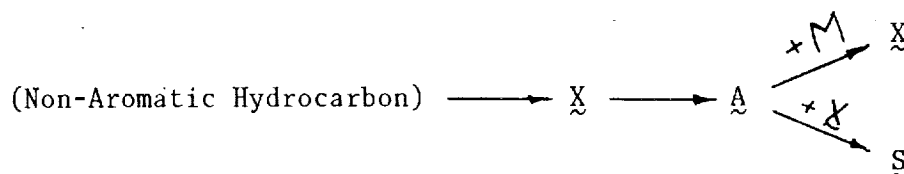
STATUS:

As a result of our activity in recent years, a conceptual model for soot formation during the pyrolysis of aromatic hydrocarbons was developed. Last year, a conceptual model for soot formation during pyrolysis of non-aromatic hydrocarbons was completed (Figure 1). It was suggested that the incipient soot formation from hydrocarbons must follow the route of consecutive production of conjugated reactive structures. The difference in soot formation characteristics between various hydrocarbons is determined by the initiation process, i.e. by the reaction leading to these reactive structures.

Soot formation in toluene-oxygen-argon and acetylene-oxygen-argon mixtures was investigated to study soot formation properties in a combustion environment. Figures 2 and 3 show typical results obtained with both fuels. The results are currently being analyzed. The preliminary observations are: a) at high concentration, oxygen completely suppresses soot formation, and b) at relatively low oxygen concentration, the addition of oxygen suppresses soot formation at higher temperatures whereas at lower temperatures oxygen promotes soot production. The observed behavior may indicate that oxidation reactions compete with ring fragmentation.

FIGURE 1:

A CONCEPTUAL MODEL FOR SOOT FORMATION DURING PYROLYSIS OF HYDROCARBONS



where:

$\tilde{X} = \{X_1, X_2, \dots\}$  is the collection of aliphatic intermediates;

$\tilde{A} = \{A_1, A_2, \dots\}$  is the collection of aromatic species;

$\tilde{S} = \{S_1, S_2, \dots\}$  is soot.

Starting from a Non-Aromatic Hydrocarbon:

The products,  $\tilde{X}$ , formed during the pyrolysis of the initial hydrocarbon, interact with each other and eventually form the aromatic species  $\tilde{A}$ .

Interaction of nascent  $\tilde{A}$  with  $\tilde{X}$  leads to soot.

Starting from an Aromatic Hydrocarbon:

Fragmentation of aromatic rings produces  $\tilde{X}$ . Interaction of intact aromatic rings with the aliphatic fragments leads to soot.

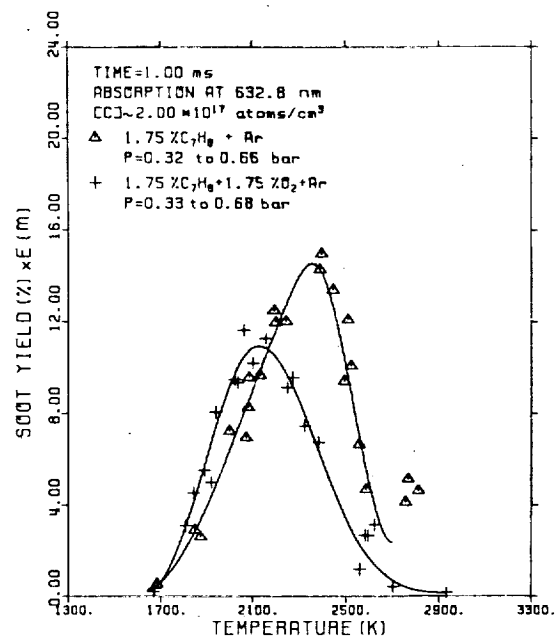


FIGURE 2:

SOOT YIELDS AT TOLUENE MIXTURES

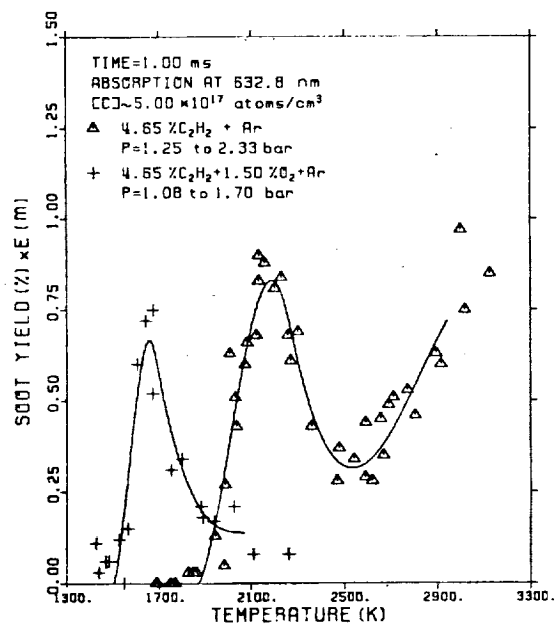


FIGURE 3:

SOOT YIELDS IN ACETYLENE MIXTURES



## SINGLE-PULSE SHOCK TUBE PYROLYSIS OF TOLUENE AND 1,3-BUTADIENE

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33775  
p. 3

## OBJECTIVE:

To investigate the rate limiting chemical mechanisms leading to the formation of soot precursors.

## BACKGROUND:

Soot production in aircraft gas turbines effects burner and turbine blade lifetimes and plume visibility. Production rates are likely to increase due to projected changes in fuels (lower H to C ratios) and engines (higher operating pressures). To assist in future engine development and modification, models are being constructed. Current versions of these models predict that the steps leading to the formation of soot precursors may be rate limiting processes; yet, neither these rate limiting steps nor their rates are known.

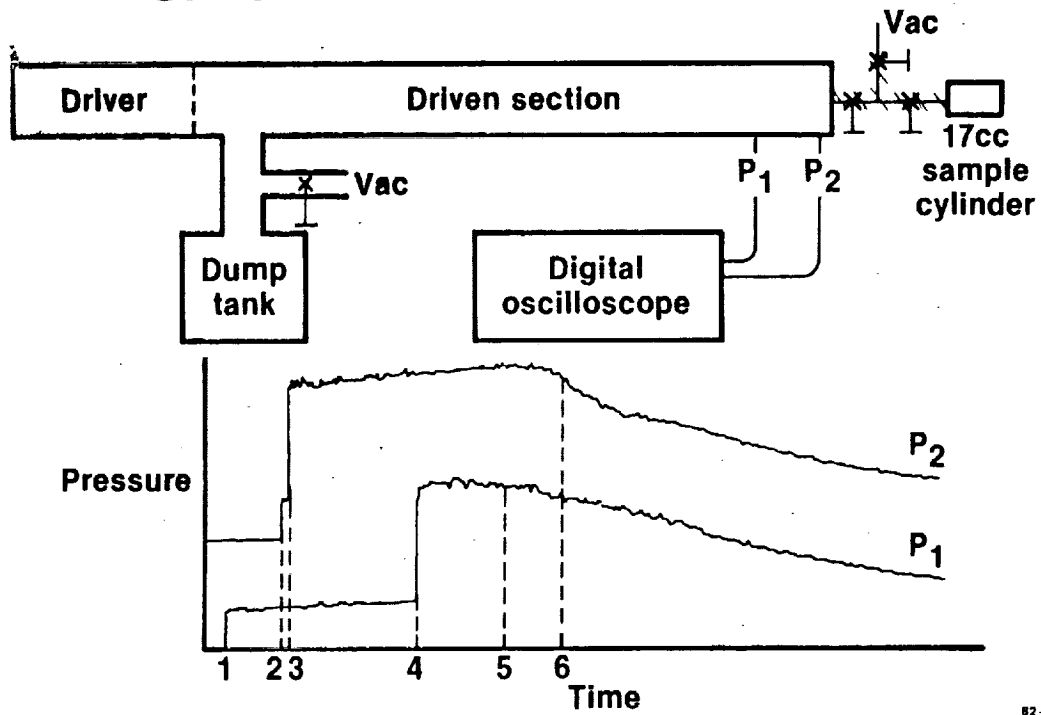
## APPROACH:

A single-pulse shock tube (see Fig. 1) is being used to collect gas samples of stable intermediates and end products of hydrocarbon pyrolysis. These gas samples are analyzed quantitatively using gas chromatography and any mass imbalance is believed to be due to the formation of PAHs and soot. Experimental decomposition rates of the parent hydrocarbon are determined and compared to predictions from the literature. Detailed chemical kinetic mechanisms describing hydrocarbon pyrolysis are being developed and models of soot formation are being compared with the experimental results. Information developed from these pyrolysis studies will provide the fundamental understanding for modeling subsequent oxidation experiments.

## STATUS:

Toluene and 1,3-butadiene have been pyrolyzed under conditions ranging from 0.016 to 1.75% in argon, 7-12 atmospheres, and 1200 to 2800 K. Toluene pyrolysis can be well described using known mechanisms and literature values for rate constants. The mechanisms demonstrate that the pyrolysis is controlled by the long-lived radical, benzyl, whose stability is enhanced via resonance. Soot production (see Fig. 2a), as indicated by the mass imbalance, is substantial, shows identical features to those observed in experiments using optical techniques, and also exhibits a strong concentration dependence. In the case of 1,3-butadiene pyrolysis, soot production (see Fig. 2b) is negligible and also is in agreement with the optical studies. The experimental rate of butadiene decomposition, however, differs from predictions from the literature. Reasons for these differences and the explanations for the different sooting potential of toluene and butadiene are being examined. For comparison with the curves of soot production, dotted lines are shown in Figs. 2a and b indicating final normalized concentrations of the reactant as a function of temperature. All data were obtained for dwell times ranging from 600 to 900 microseconds.

# SINGLE-PULSE SHOCK TUBE



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Fig. 2a

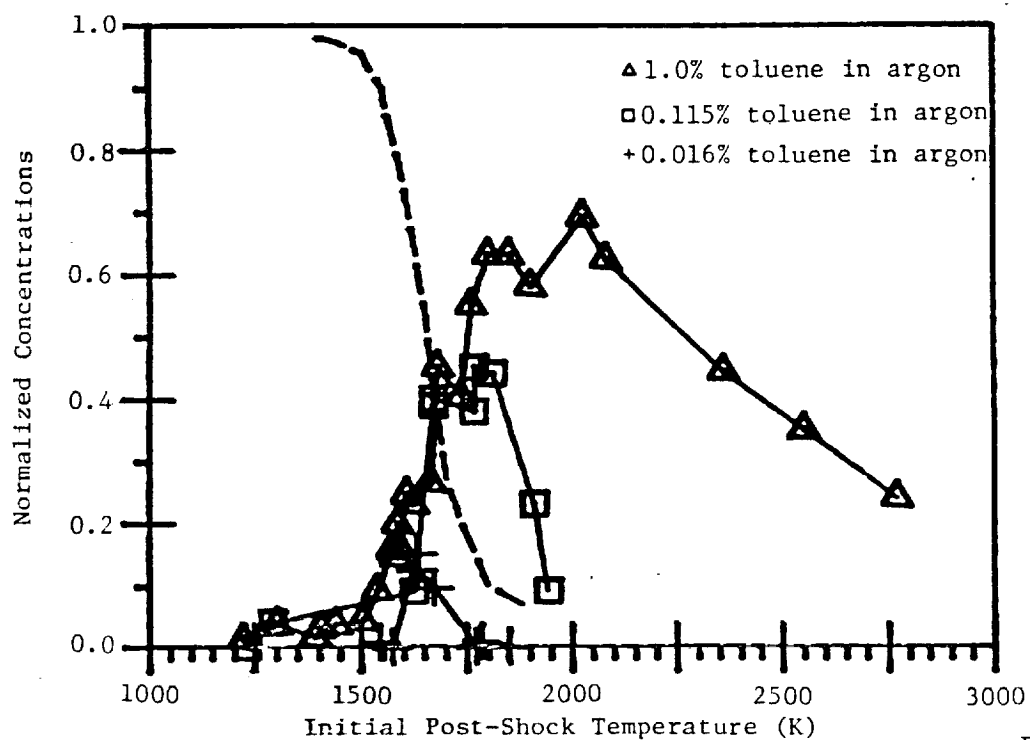
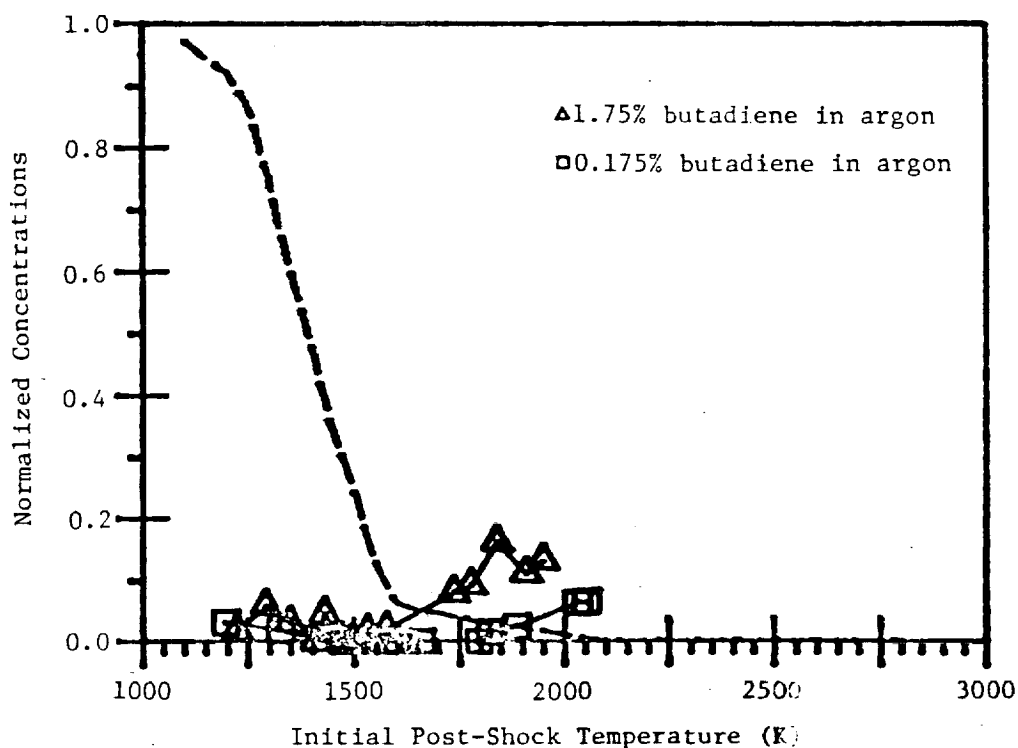


Fig. 2b



Figs. 2a and b. Post-shock normalized concentrations of soot and reactants. Symbols represent normalized soot concentrations which are equated to the concentrations of missing carbon and possibly includes undetected PAHs. Dotted lines represent final normalized concentrations of reactant and are essentially independent of initial concentration.



SHOCK TUBE MEASUREMENTS OF THE BRANCHED-CHAIN  
MECHANISM FOR THE ETHANE-CARBON MONOXIDE-OXYGEN SYSTEM

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OBJECTIVE:

Modern computers have the capability of modeling practical combustion systems by combining the equations of chemical kinetics, fluid mechanics, and thermodynamics. To exploit this capability, a detailed knowledge of reaction mechanisms and rates is required. The aim of this research is to obtain fundamental rate data on elementary reactions important in the combustion of hydrocarbons.

BACKGROUND:

The high temperature oxidation of hydrogen, carbon monoxide, and hydrocarbons is characterized by chainbranching reactions. When a fuel-oxygen mixture is subject to a pulse of temperature and pressure in a shock tube, atom and free radical concentrations - H, OH, O, etc. - grow exponentially. For example

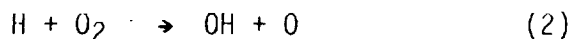
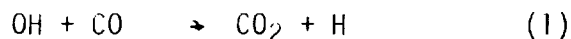
$$(O) \propto \exp(\lambda t)$$

where (O) is the concentration of oxygen atoms, t is time, and  $\lambda$  is called the growth constant.

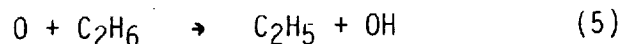
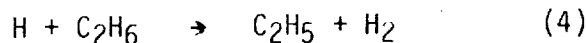
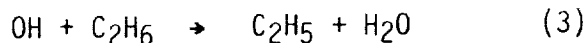
Previously, rate data on hydrogen, carbon monoxide, and methane oxidation have been obtained from growth constants obtained by measuring the exponential growth of CO flame band radiation in the shock tube which monitors the oxygen atom concentration. The data were analyzed using analytic solutions to the ignition kinetics.

APPROACH:

The oxidation of carbon monoxide proceeds through the reactions



If this reaction scheme is to branch, the oxygen atom produced in the second reaction must react to produce another atom or radical. Accordingly, by adding small amounts of ethane to carbon monoxide-oxygen mixtures, we hope to obtain information on the rates of the reactions



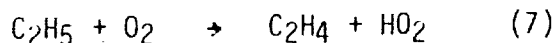
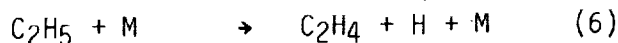
from growth constants obtained with the Lewis shock tube.

#### STATUS:

Growth constants have been measured for two mixtures. The data and compositions are shown in Figure 1.

An analytic solution to the kinetics was obtained using reactions (1) - (5). When rate data from the literature were used, solutions were not chainbranched; reactions (3) and (4) served as chain terminations.

Chainbranching solutions have been obtained by adding the reactions



Computed growth constants are shown as lines in Figure 1. The calculated growth constants agree with experimental values for the mixture with 15% oxygen but not for the mixture with 0.55% oxygen.

When the scheme of reactions was expanded to include



or



followed by



computed growth constants were changed only slightly.

A sensitivity analysis shows that computed growth constants for 0.55%  $\text{O}_2$  mixture are most sensitive to the rates of reactions (2) and (5). The rate of reaction (2) is well established. If the rate of reaction (5) is adjusted to fit the data, a rate constant with an absurdly large preexponent factor is obtained; orders of magnitude larger than collision frequency.

The next step will be to explore other channels for H and O atom reactions, for example



followed by



and

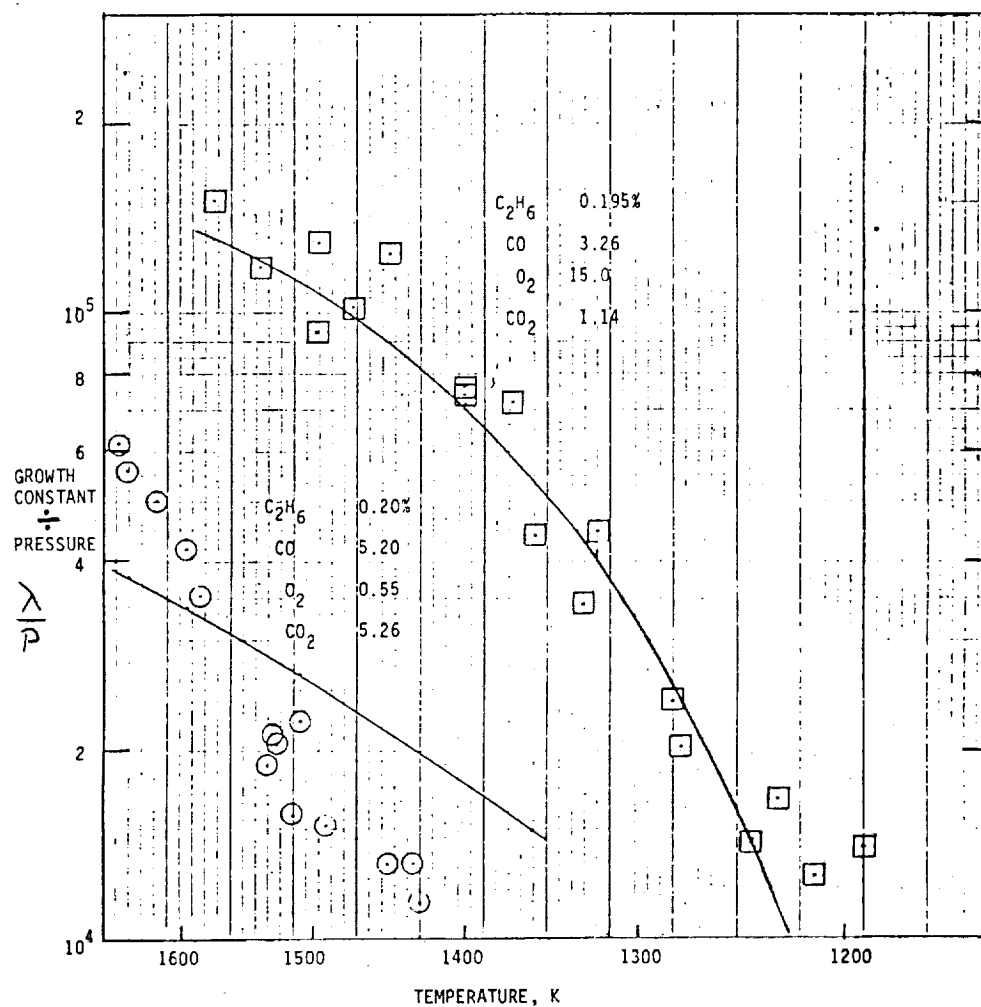


FIGURE 1 EXPERIMENTAL AND CALCULATED GROWTH CONSTANTS



## ROLE OF THE HYDROXYL RADICAL IN SOOT FORMATION

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p. 3

1. Objective:

The goal of this project is to determine the role of the hydroxyl radical during formation of soot. Correlations will be sought between OH concentration and (1) the critical equivalence ratio for incipient soot formation and (2) soot yield as a function of higher equivalence ratios. The ultimate aim is the development of a quasi-global kinetic model for the pre-particulate chemistry leading to soot nucleation.

2. Background:

The proper design of internal combustion engines, gas turbines, and stationary sources requires knowledge of soot formation kinetics to maximize material lifetime and thermal efficiency while simultaneously minimizing pollutant production. As fuel aromaticity increases, formation of polycyclic aromatic hydrocarbons (PAH) and soot becomes more problematic. PAHs could, in fact, be soot precursors. Higher fuel aromaticity may also favor the production of those PAH compounds known to be carcinogenic. Such compounds often condense on the surface of soot particles during combustion processes creating a public health problem since the size range of the particles allows ingestion deep into the respiratory tract. Excessive soot formation is also indicative of inefficient energy conversion and, in practical systems, soot particles can cause excessive wear and local hot spots.

3. Approach:

Hydroxyl radical concentration profiles are measured directly in both laminar premixed and diffusion flames using the newly developed technique, laser saturated fluorescence (LSF). This method is capable of measuring OH in the presence of soot particles. Aliphatic and aromatic fuels will be used to assess the influence of fuel type on soot formation. The influence of flame temperature on the critical equivalence ratio and soot yield will be related to changes in the OH concentration profiles. LSF measurements will be augmented with auxiliary measurements of soot and PAH concentrations to allow the development of a quasi-global model for soot formation.

#### 4. Status:

Low pressure premixed flames have been stabilized using the existing flat flame burner and problems with soot deposition on pressure vessel windows have been overcome. Figure 1 shows data collected in 20 Torr acetylene-oxygen flames at an unburned gas velocity of 50 cm/sec and at equivalence ratios ( $\phi$ ) of 1.0 - 3.5. The so-called standard acetylene-oxygen flame occurs at  $\phi = 3.5$ . The critical equivalence ratio for the onset of sooting is observed to be between  $\phi = 2.0$  and  $\phi = 2.5$ . The transition to sooting flames is continuous with respect to  $\phi$  and no abrupt change in the OH concentration profile occurs near the onset of soot formation. The fluorescence signal is free from any interference due to the presence of soot or PAHs in these flames.

Correlations have been developed using literature data to relate the critical equivalence ratio  $\phi_c$  at which soot just begins to form to the OH number density at chemical equilibrium. Figure 2 shows the derived relationship between  $\phi_c$ , normalized to a standard temperature of 2000 K, and  $\log [\text{OH}]_{eq}$ . Note that  $\phi_c$  (2000 K) is independent of temperature and reflects only the fuel molecular structure. The effect of fuel type on soot formation appears to be well correlated by

$$\phi_c(2000\text{K}) = \alpha - \beta \log [\text{OH}]_{eq}$$

where  $\alpha$  and  $\beta$  are constants dependent on fuel type - alkenes, alkanes, and aromatics. A preliminary quasi-global model for precursor formation and oxidation has been developed based on the results demonstrated in Figure 2.



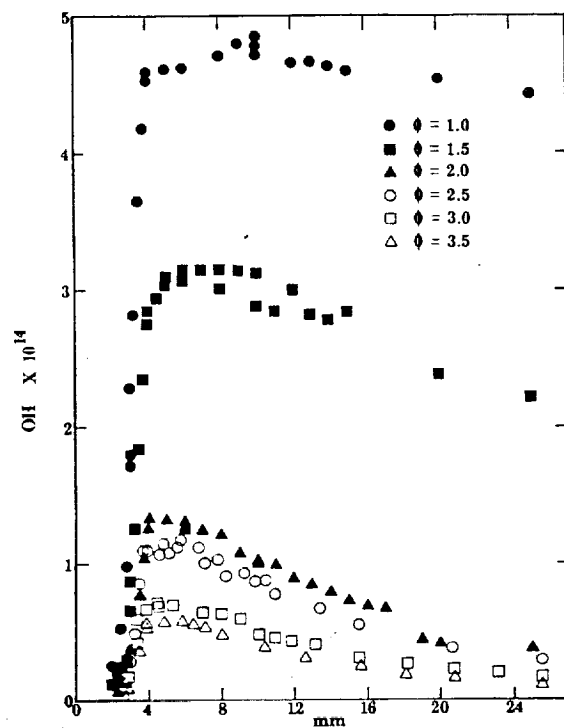


Figure 1: Data collected in 20 Torr acetylene-oxygen flames at equivalence ratio of 1.0 - 3.5.

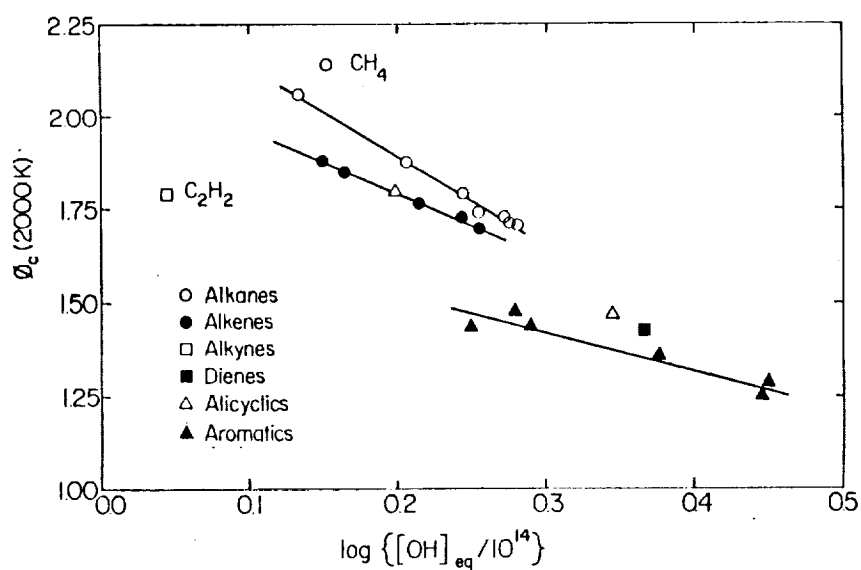


Figure 2: The derived relationship between the critical equivalence ratio normalized to a standard temperature of 2000 K and  $\log [\text{OH}]$ .



ANALYTIC MODELING OF SOOT NUCLEATION  
UNDER FUEL RICH CONDITIONS

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P-6I. OBJECTIVE

The objective of the present research is to construct a soot nucleation model according to a proposed chemical kinetic scheme to delineate quantitatively the nucleation mechanism in the soot formation process.

II. BACKGROUND

Sooting is a highly undesirable feature in engine combustion from many points of view including environmental considerations and power plant efficiencies. It is expected, naturally, the understanding of the fundamental soot formation mechanism may lead to more efficient engine design with lower particulate emissions. Unfortunately, such mechanism has not been clearly established despite voluminous literature reporting the theoretical and experimental research related to it. The current investigation represents another effort from a new point of view to achieve such a basic understanding.

III. APPROACH

Instead of following the traditional views which generally associate sooting with the homogeneous nucleation process in phase transformation or polymerization, we choose a chemical kinetic approach. In our proposed scheme the number of carbon atoms in the intermediate species between the fuel molecule and soot nuclei is continuously increased by radical additions. The number of hydrogen atoms in the intermediate species on the other hand is steadily decreased by radical dehydrogenation. When the number of carbon atoms in each of the intermediate molecules has exceeded a certain limit and the number of hydrogen atoms has fallen below a certain level, they may coagulate with one and another to form a larger molecule which is regarded as the initial soot nuclei in the present theory. Further coagulation and surface growth of the nuclei will lead to observable soot particles.

IV. STATUS

A mathematical model based on a postulated kinetic scheme has been constructed. Numerical calculations have been performed under conditions of shock tube experiments and premixed flat flames with  $C_2H_2$ ,  $C_6H_6$ ,  $C_4H_{10}$ , etc. used as fuels. Results have shown that many important characteristics associated with the sooting process such as the extremely fast reaction rate, smoke point of fuels, temperature and pressure effects on smoke points, etc. are predicted by the calculations of the model. Graham, et al. based on results of their shock tube work suggested a two channel mechanism for the carbon formation process. Our calculations have confirmed the validity of this proposal. Selected results of numerical calculation are presented in Figs. 1-10. The growth and coagulation process of soot nuclei is also under current investigation. A mathematical model is being constructed to complete the kinetic path of soot nuclei produced in the nucleation model to grow and become measurable soot particles.

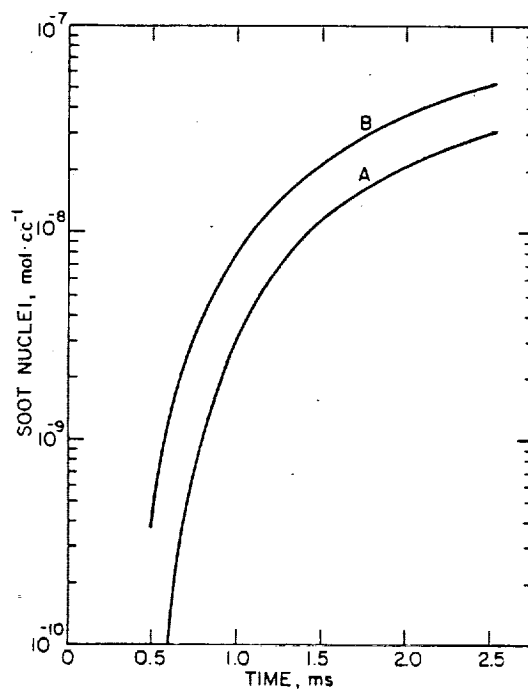


Fig. 1. Calculated soot nuclei trajectory  
 Fuel:  $C_2H_2$ ,  $P = 760$  mm, C atom density =  $4.6 \times 10^{18}$  atoms.cc $^{-1}$   
 A:  $T = 1600^\circ K$  and B:  $T = 2200^\circ K$

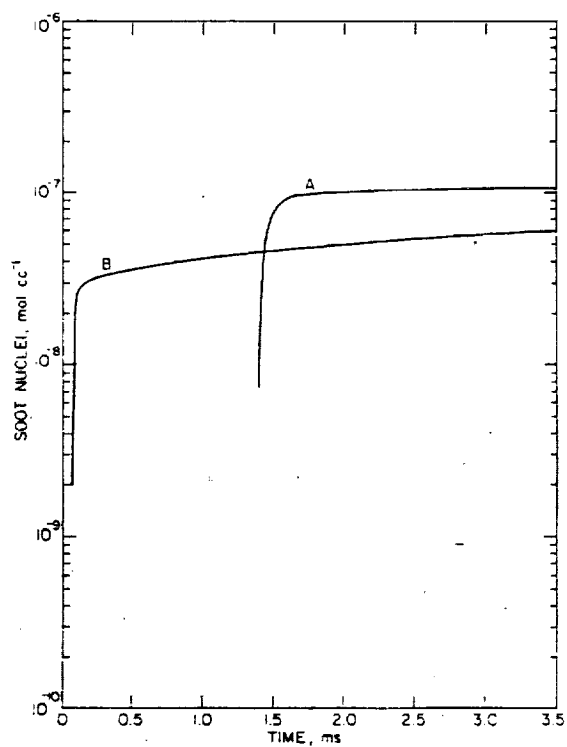


Fig. 2. Calculated soot nuclei trajectory  
 Fuel:  $C_6H_6$ ,  $P = 760$  mm, C atom density =  $1.3 \times 10^{18}$  atoms.cc $^{-1}$   
 A:  $T = 1600^\circ K$  and B:  $T = 2200^\circ K$

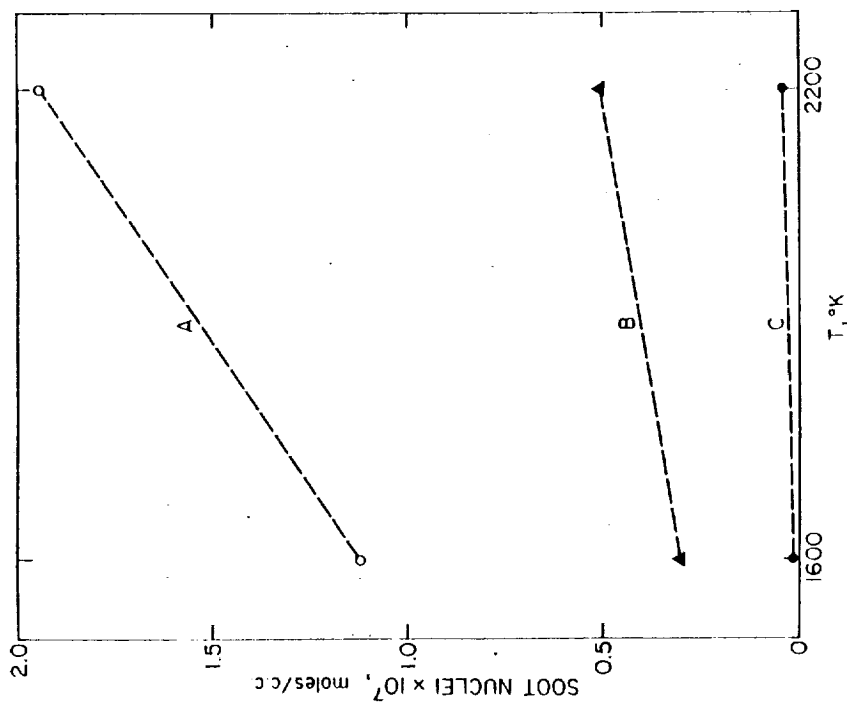


Fig. 3. Temperature effect on soot nuclei yield  
 Fuel:  $C_2H_2$   
 A:  $P = 1520$ mm, C atom density =  $9.2 \times 10^{18}$  atoms.cc<sup>-1</sup>  
 B:  $P = 760$ mm, C atom density =  $4.6 \times 10^{18}$  atoms.cc<sup>-1</sup>  
 C:  $P = 300$ mm, C atom density =  $1.8 \times 10^{18}$  atoms.cc<sup>-1</sup>

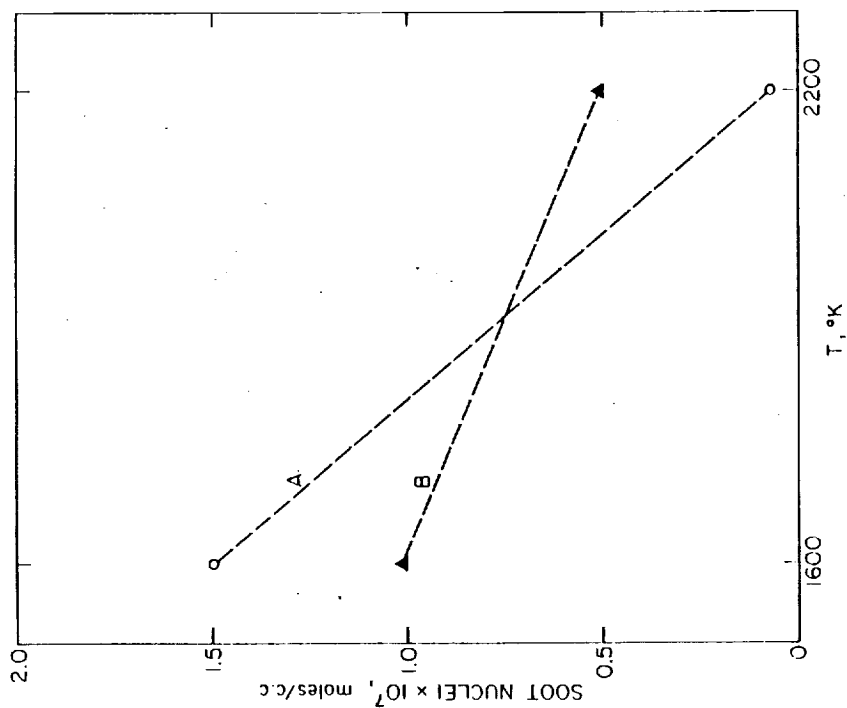


Fig. 4. Temperature effect on soot nuclei yield  
 Fuel:  $C_6H_6$   
 A:  $P = 1000$ mm, C atom density =  $1.7 \times 10^{18}$  atoms.cc<sup>-1</sup>  
 B:  $P = 760$ mm, C atom density =  $1.3 \times 10^{18}$  atoms.cc<sup>-1</sup>

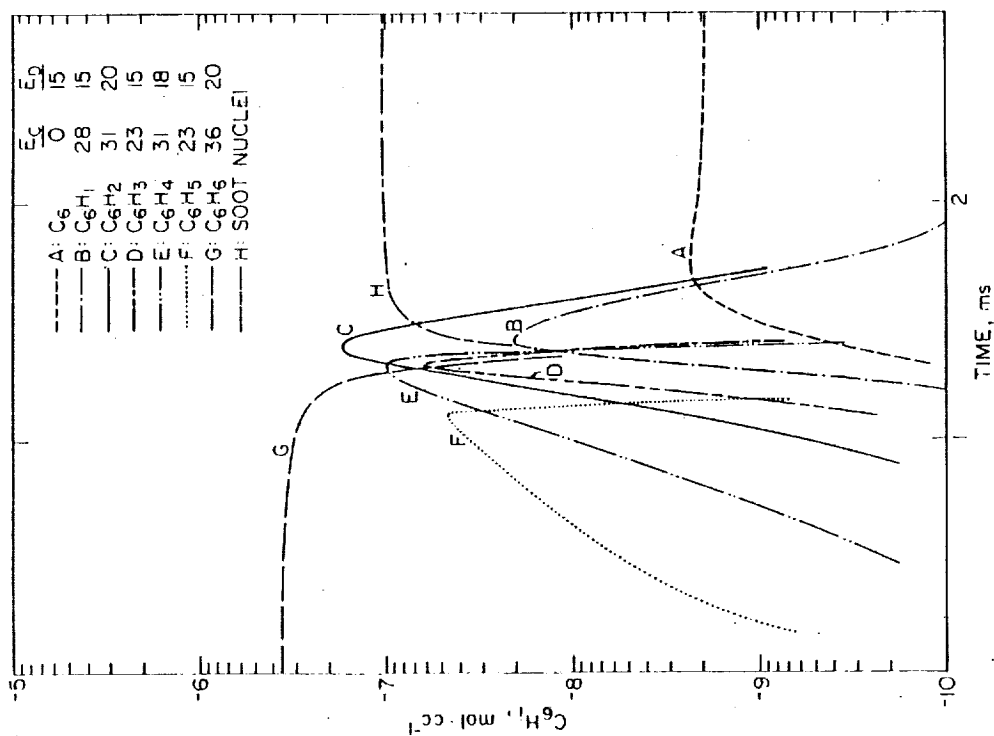


Fig. 5. Trajectories of selected intermediate species with 6 carbon atoms formed in a shock wave.  
 Fuel:  $C_6H_6$ ,  $P = 760\text{mm}$ ,  $T = 1600^\circ\text{K}$  and  
 C atom density -  $1.3 \times 10^{18}$  atoms. $\text{cc}^{-1}$

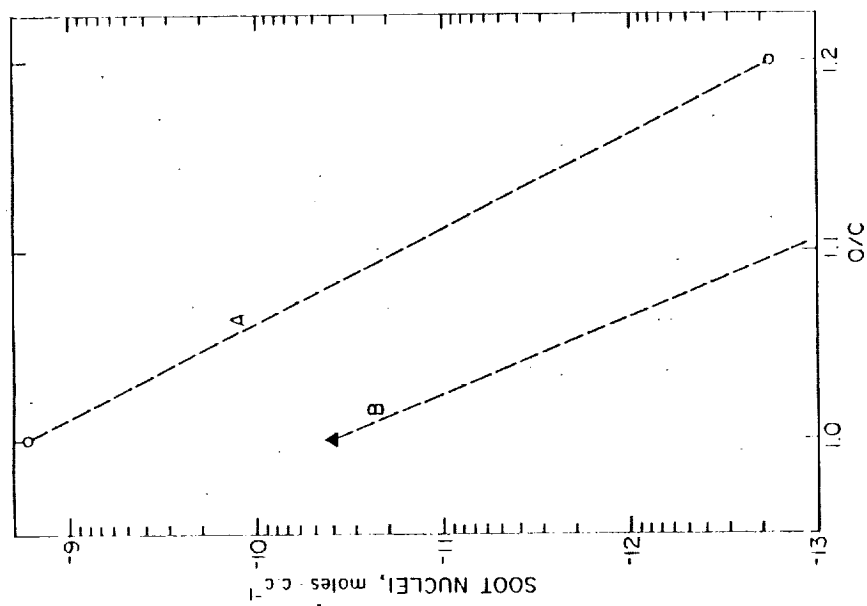


Fig. 6. Pressure effect on smoke point  
 Fuel:  $C_2H_2$  A:  $P = 1520\text{mm}$  B:  $P = 760\text{mm}$

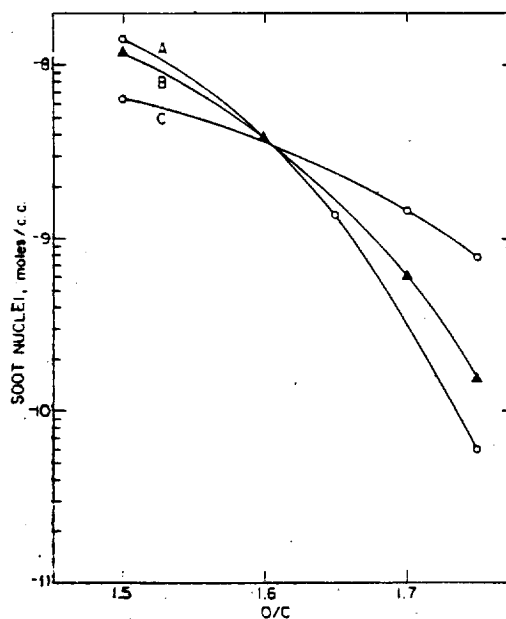


Fig. 7. Pressure effect on smoke point  
 Fuel:  $C_6H_6$       A: P = 300mm  
                               B: P = 760mm  
                               P = 1000mm

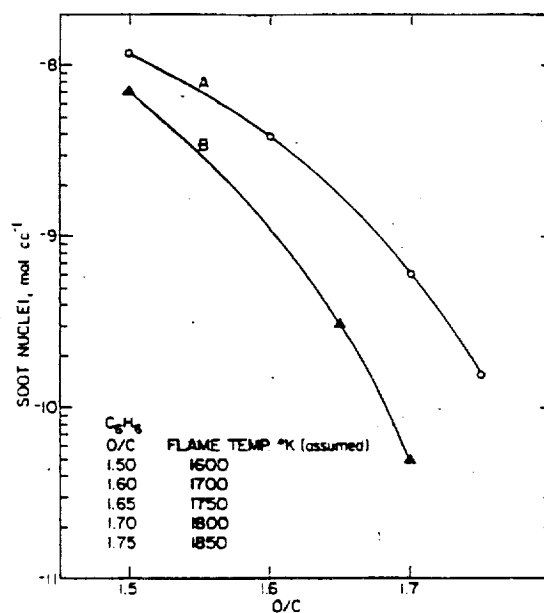


Fig. 8. Temperature effect on smoke point  
 Fuel:  $C_6H_6$       A: assumed flame temperature  
                               B: 200°K above assumed flame temperature

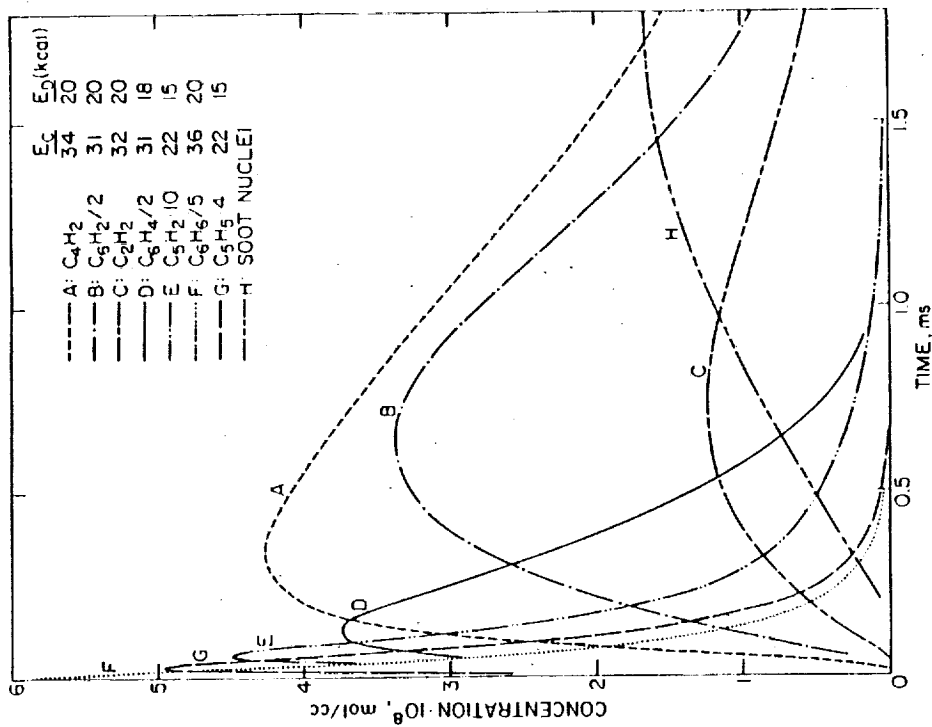


Fig. 9. Trajectories of selected intermediate species in a sooting  $C_6H_6$  flame.  
O/C = 1.5, P = 760mm and T = 1600°K

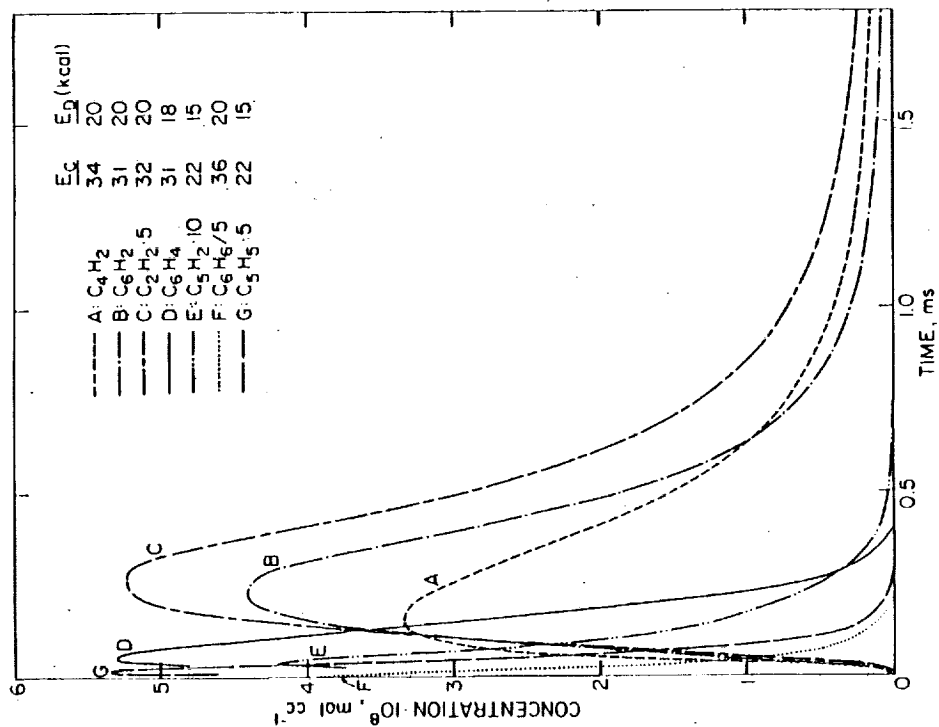


Fig. 10. Trajectories of selected intermediate species in a non-sooting  $C_6H_6$  flame.  
O/C = 1.8, P = 760mm and T = 1900°K



## OXIDATION KINETICS AND SOOT FORMATION

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p. 5

## RESEARCH OBJECTIVE:

To clarify the role of aromaticity in the soot nucleation process by determining the relative importance of phenyl radical/molecular oxygen and benzene/atomic oxygen reactions in the complex combustion of aromatic compounds.

## BACKGROUND:

The major oxygenated intermediate detected in flow reactor studies of the high temperature oxidation of benzene is phenol. Two reactions have been suggested as responsible for the presence of phenol: 1) phenyl radical reaction with molecular oxygen to form a phenoxy radical (which is detected as phenol) and oxygen atom and; 2) the addition of atomic oxygen to benzene followed by the rearrangement of the adduct to form phenol. If indeed the phenoxy radical is formed during the oxidation of benzene, then the ring rupture sequence would proceed quickly and involve some radical species that are known to be important in the sooting process. If on the other hand, phenol is formed directly, a series of slower steps involving less reactive stable species may be involved in the ring rupture process. The existence of two paths for the formation of the same detected product, phenol, creates a kinetic mechanistic dilemma whose resolution may clarify the manner in which aromatics contribute to fuel sooting.

## APPROACH:

Three sets of chemical flow reactor experiments have been designed to determine the relative importance of the phenyl radical/molecular oxygen and benzene/atomic oxygen reactions. The essential elements of these experiments are 1) the use of cresols and anisole formed during the high temperature oxidation of toluene as chemical reaction indicators; 2) the in situ photolysis of molecular oxygen to provide an oxygen atom perturbation in the reacting aromatic system and; 3) the high temperature pyrolysis of phenol, the cresols and possibly anisole.

## PROGRESS:

The Princeton University turbulent flow reactor shown in Figure 1 was used for studies of the oxidation of toluene under fuel lean,  $\phi = 0.63$ , and fuel rich,  $\phi = 1.4$ , conditions. Species concentration profiles as a function of time from these experiments are displayed in Figures 2 and 3. Particular attention has been paid to the identification and quantification of the cresols. Meta-cresol was found in the highest concentration suggesting quite strongly that oxygen atom addition to the aromatic ring of toluene is taking place early in the combustion process. The absence of any methyl-cyclopentadiene suggests, though, that the decomposition of the cresols at the conditions of the toluene oxidation does not lead directly to ring rupture. The data in Figures 2 and 3 do indicate, however, that the cresols decompose, if not to methyl-cyclopentadiene and carbon monoxide, then conceivably to benzene or back to toluene.

In order to better understand the processes involved in the high temperature decomposition of phenol and the cresols, a pyrolysis study of phenol was started. In the first part of this study solid phenol was dissolved in benzene. It has been shown by flow reactor experiments that benzene does not decompose at approximately 1200 K and can serve as a convenient carrier liquid for phenol. The solution of phenol and benzene was then vaporized and introduced into the flow reactor. The results from one such phenol pyrolysis study at 1183K are shown in Figures 4, 5 and 6.

The data indicate that the decay of phenol is attended by the production of unequal amounts of carbon monoxide and cyclopentadiene and that the carbon monoxide formed does not equal the amount of phenol that has decayed. The fact that there is less cyclopentadiene than carbon monoxide can be attributed to subsequent pyrolysis of the cyclopentadiene. The presence of acetylene, ethylene and methane confirms this possibility. The observation that the amount of CO formed is only about one half of the amount of phenol that has disappeared can only mean that another decomposition path is present, possibly forming benzene. The existence of such a path may mean that a large portion of the phenol formed by O atom addition to the benzene ring during oxidation may return to benzene and not take part in ring decomposition!

#### FUTURE WORK:

The quartz reactor tube in the flow reactor has now been modified to permit optical access, so that the development of the photolytic O atom perturbation technique is being pursued actively. Optical light sources are under study as are chemical titration techniques necessary to measure quantitatively the O atom concentration. Actual experimentation will begin in the next grant year and this aspect of the program will be the primary focus for the coming years.

Working with corrosive phenol has posed many experimental problems, but these now have been mostly resolved. More definite experiments with phenol and the cresols will be pursued actively in order to follow up some of the exciting ideas that have come out of the preliminary work on phenol pyrolysis.

Also during the coming year, the toluene work will be extended particularly to obtain more data around stoichiometric.

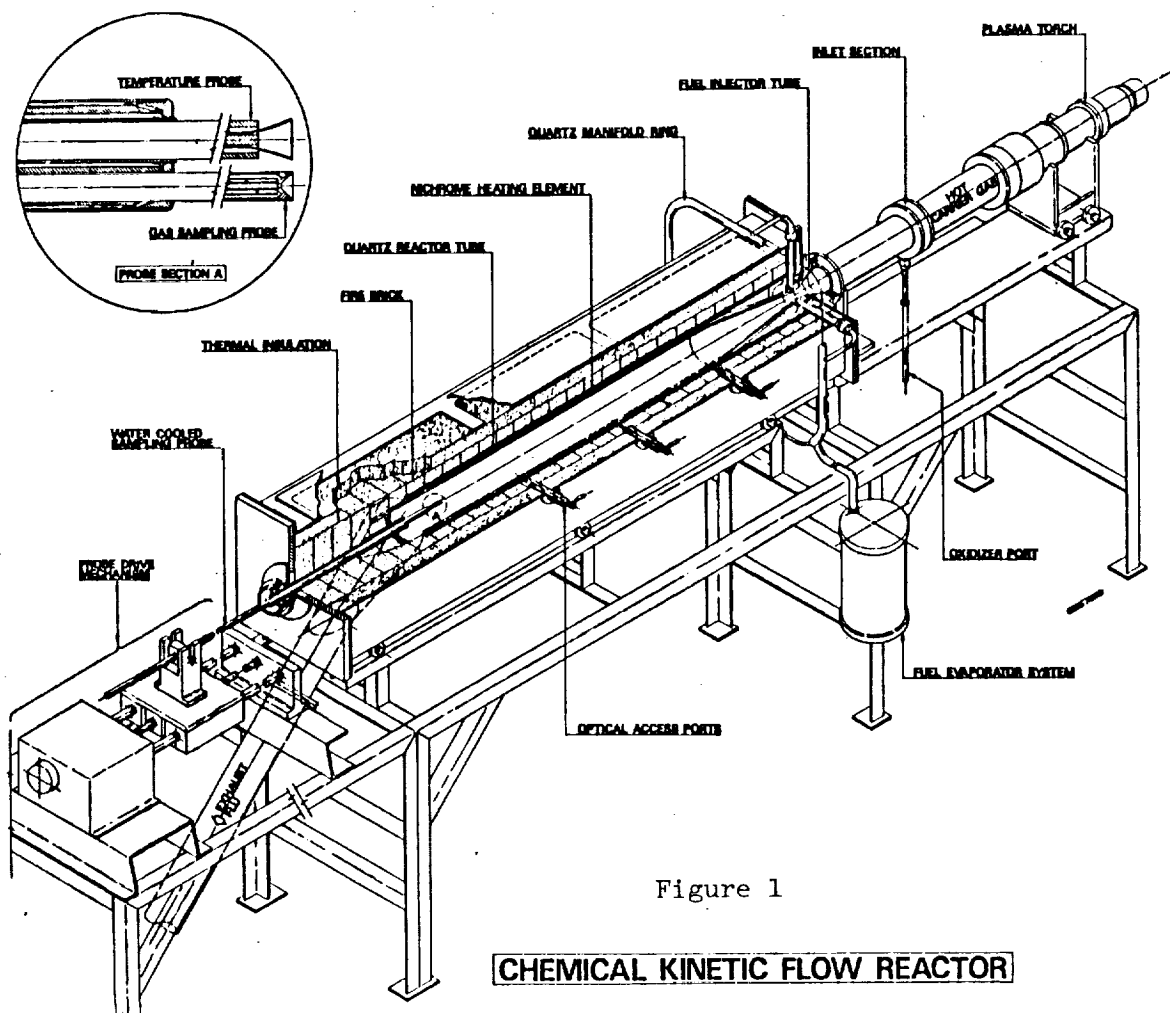


Figure 1

# CHEMICAL KINETIC FLOW REACTOR

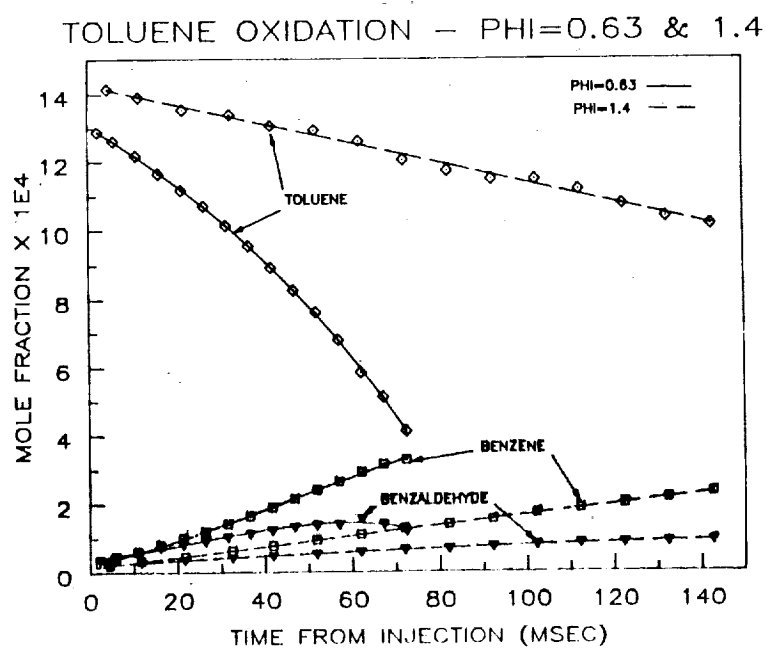


Figure 2

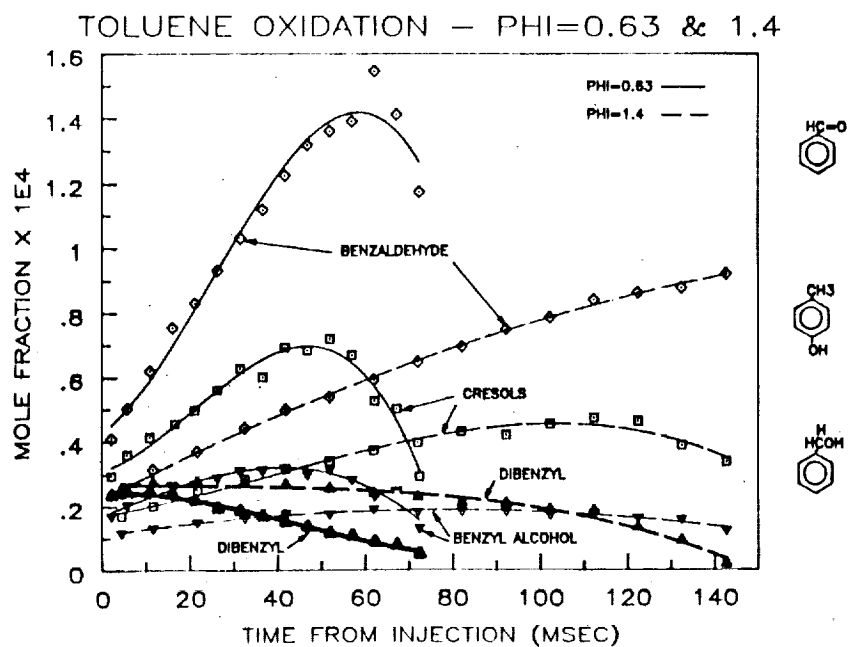


Figure 3

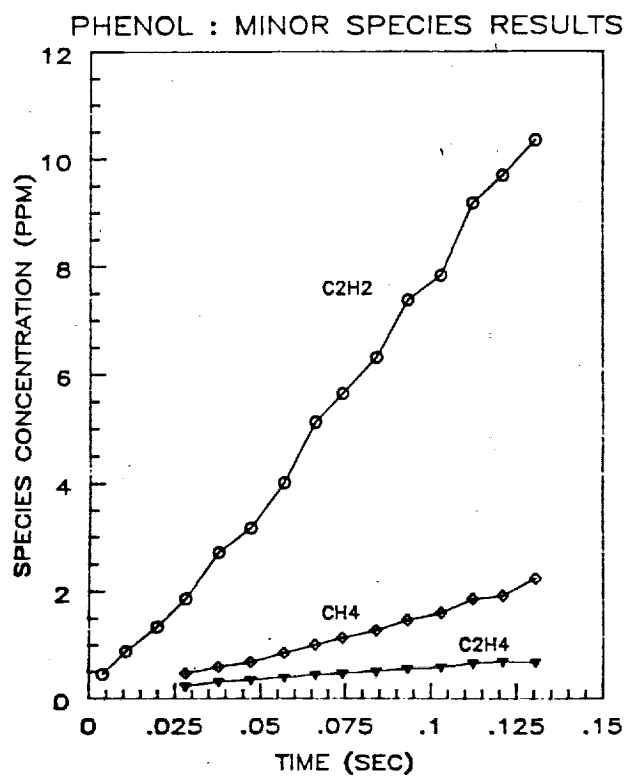


Figure 4

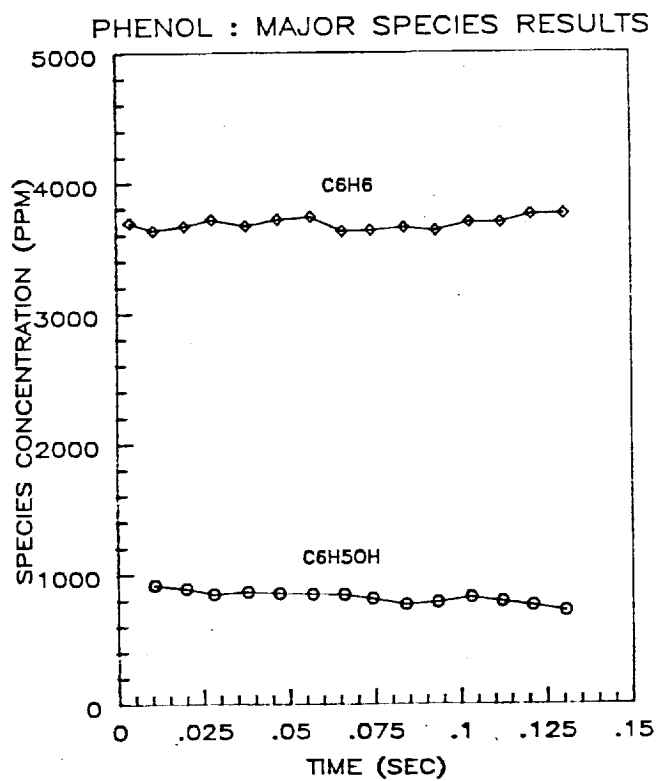


Figure 5

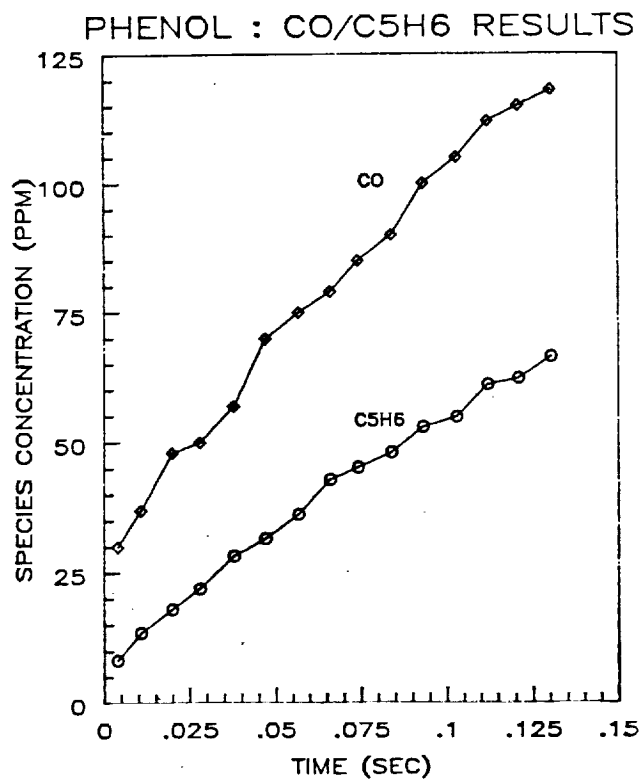


Figure 6



## CATALYTIC OXIDATION OF VERY FUEL RICH MIXTURES

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P-4

OBJECTIVE:

To demonstrate the feasibility of using a catalytic reactor as a tool to study soot formation from the fuel rich side of the soot limit ( $\phi = 3 - 6$ ).

BACKGROUND:

Soot formation in a gas turbine combustor is a problem that is expected to get worse as the quality of jet fuel decreases. This increased soot loading will have adverse effects on liner temperature and meeting environmental standards. Thus it has become important to develop models which will explain the formation of soot and the effect fuel structure has on it. This has prompted a renaissance of research in flames, shock tubes, and flow reactors on the mechanism of the formation of soot.

Street and Thomas studied the formation of carbon in pre-mixed flames and observed that carbon (soot) was not formed when the composition of the test gas was near the rich limit. They proposed that the reason for this behavior was that the rate controlling step has a high activation energy, and thus, the rate of carbon formation would be low at these temperatures. This suggests that soot formation could be studied from the fuel rich side of the soot limit where sampling and test conditions would be easier to control.

APPROACH:

The experimental approach to be taken in the first phase of the research is to document that a hydrocarbon fuel can be burnt at very rich equivalence ratios without forming soot. A simple mono-component fuel, iso-octane, will be used as the test fuel. To insure that combustion is uniform across the catalyst bed, measurements will be made of the fuel-air equivalence ratio profile across the inlet and the temperature and product distribution across the outlet.

Phase II will be to use this environment as a testing ground for determining the effect the structure of a hydrocarbon fuel has on its tendency to form soot. Various amounts of organic compounds such as benzene will be added to the iso-octane and the reaction products studied. Other compounds to be tested will be xylene, toluene, and naphthalene.

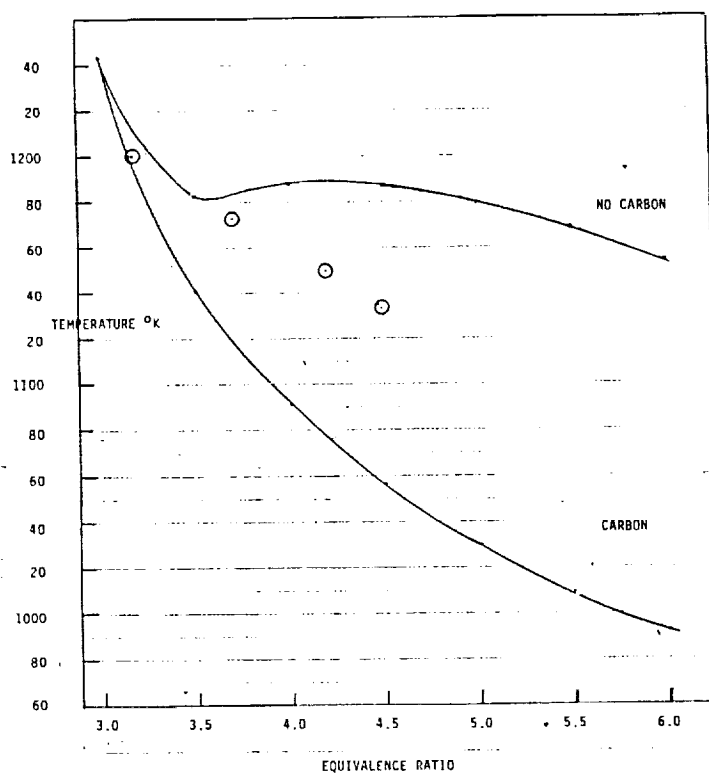
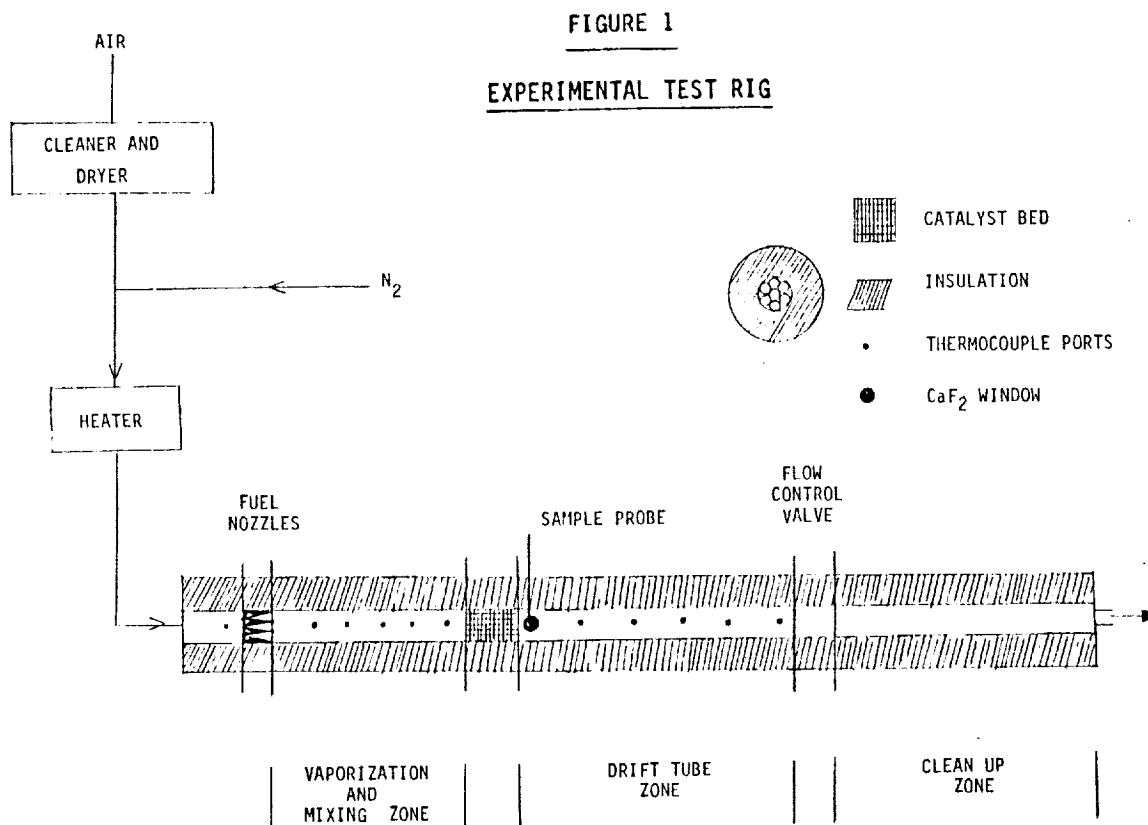
## STATUS:

An experimental rig (Figure 1) was built to catalytically oxidize a hydrocarbon fuel at equivalence ratios well beyond the rich limit. Catalysts were required because the oxidation rates are slow at these temperatures. A platinum-palladium catalyst proved to be excellent for this type of work. The preliminary data are very interesting and indicate that soot-free combustion at high equivalence ratios, 3.3. to 4.5 for iso-octane, appears to be feasible. Product gas temperatures were compared with equilibrium temperatures calculated by first, allowing carbon to form and second, by not allowing it to form. These results are shown in Figure 2 where the temperature is plotted vs the equivalence ratio. Collected gas samples were analyzed for  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ,  $C_2H_6$ ,  $C_2H_4$ , and  $C_2H_2$ . The sum of these concentrations indicated that about 15% of the sample was higher hydrocarbons. At present, we have not been able to identify these compounds; but we have been able to separate them. Figure 3 shows two chromatograms of the reaction products. The known gases evolve in about one minute, and there are about nine or more peaks which appear after this. The peak at 14-15 minutes on the upper chromatogram is very interesting since it only becomes measurable at higher temperatures ( $\phi = 3.3$ ) where we might expect soot to start forming.

The continuation of this work will involve --

- (a) Adding more catalyst to the reactor
- (b) Determination of the unknown reaction products
- (c) Analysis of the liquid products
- (d) Broadening the range of the equivalence ratio, especially, the low end.





**FIGURE 2: REACTOR TEMPERATURE COMPARED WITH THE TWO EQUILIBRIUM CALCULATIONS**

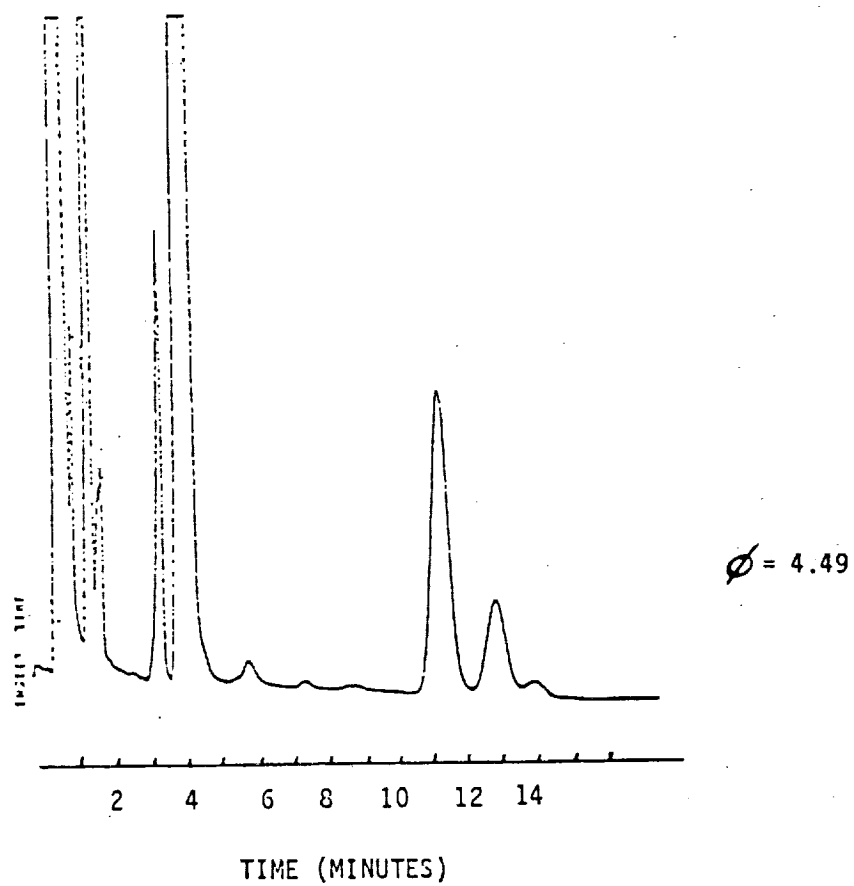
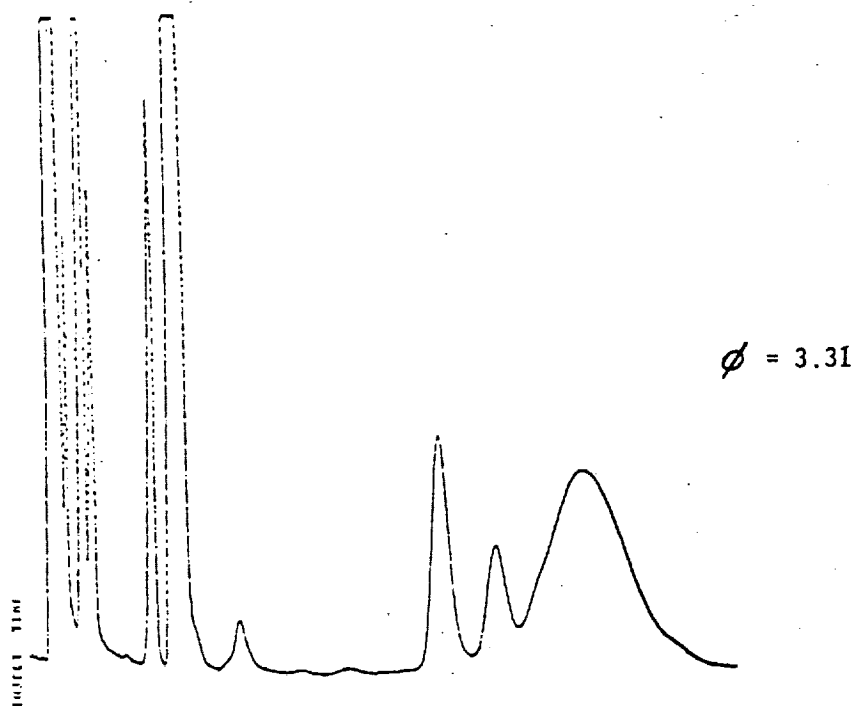


FIGURE 3: CHROMATOGRAMS OF UNDETERMINED  
REACTION PRODUCTS

# THE ROLE OF SURFACE GENERATED RADICALS IN CATALYTIC COMBUSTION

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## OBJECTIVE:

To determine whether or not, under catalytic combustion conditions, there is significant radical production by catalytic surface reactions and the effect of such radicals on the gas phase chemistry.

## BACKGROUND:

The advantages of catalytic combustion over conventional combustion are lower emissions, higher efficiency, increased operational stability, stable operation at lower equivalence ratios, improved pattern factors and wider fuel specifications. The performance of a catalytic combustor is determined by the interaction of a number of physical and chemical processes, including convection and diffusion of species, heat and momentum; conduction and radiation heat transfer in the substrate; and gas phase and surface chemical reactions. An important, and as yet unresolved, question regarding the interaction of these fundamental physical and chemical processes is the effect of catalytic surface reactions on the gas phase chemistry. In particular, it is the effect of intermediate and radical species, generated by catalytic wall reactions, on the gas phase chemistry which has not been established. That radicals can be produced by catalytic surface reactions and that at sufficiently high surface temperatures the radicals are desorbed by the surface into the gas phase has been well documented in low pressure flow experiments. However, the importance of this phenomenon in catalytic combustion and the role of these radicals in determining the performance characteristics of catalytic combustors has not been established.

## APPROACH:

The effect of surface generated OH radicals on the oxidation of propane in a platinum-coated, stacked-plate, catalytic combustor is being studied. Gas temperature and OH concentration profiles are measured at several axial locations in the 2-D flow field between two catalytic plates in the stacked plate, catalyst bed. Resonance absorption spectroscopy is used to measure both the temperature and OH concentration. In addition, the axial substrate temperature profile and the exhaust gas temperature and composition are measured using thermocouple and gas sampling probes.

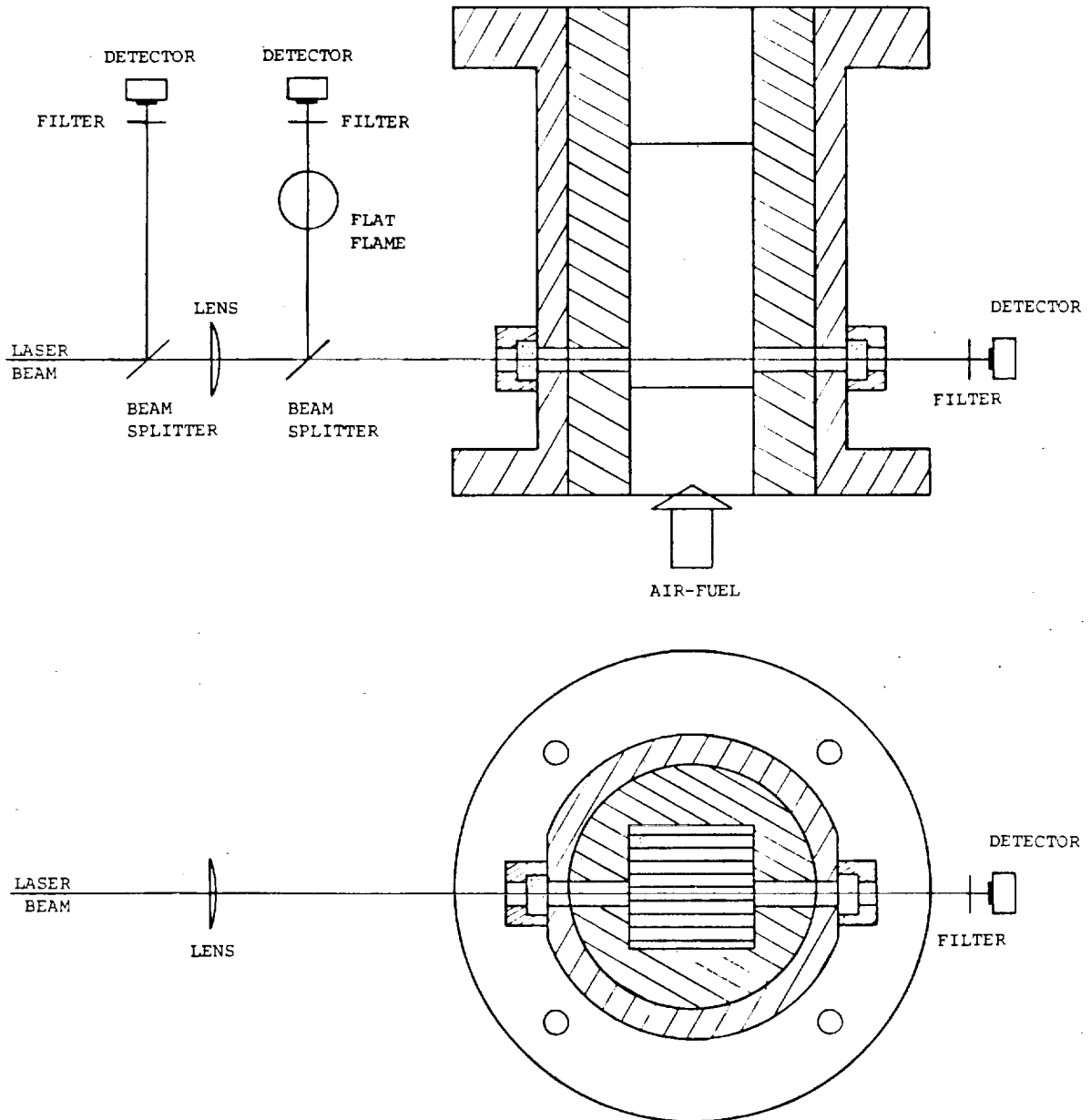
STATUS:

A new test section, design with optical access and for use with a stacked plate catalyst configuration, has been constructed. In addition, a grazing incidence configuration dye laser system has been built, where the required UV beam is obtained by frequency doubling.

Anticipating that the role of surface generated radicals will be particularly important during light-off, experiments have been conducted to characterize the catalyst's light-off response time. These tests, using hydrogen in air over a platinum-coated, stacked-plate catalyst bed, indicate that the ignition transient is of the order of 1 to 10 seconds. The laser repetition rate is 10 Hz, which means that it will be possible to temporally resolve the change in OH concentration during ignition. The hydrogen-air ignition experiments are currently being repeated and line center absorption measurements of the  $Q_1(6)$  line of OH are being made.

STACKED PLATE CATALYTIC COMBUSTOR WITH OH ABSORPTION EXPERIMENT

STACKED-PLATE CATALYST TEST SECTION





## SHOCK TUBE STUDIES OF SOOT FORMATION

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p. 4

## OBJECTIVE:

To record the time histories of the major and minor species which appear in the pyrolyses of toluene, benzene, butadiene, allene, and acetylene; to develop a set of reactions that will model the observed profiles over a wide temperature and concentration range; to identify the critical reactions that influence the pre-particle soot formation process.

## BACKGROUND:

The presence of aromatic compounds in synthetically derived fuels has focused interest on the problem of soot emission control. Flame structure studies have revealed the importance of pyrolytic reactions in the combustion process. Shock tubes have been employed to investigate the magnitude of soot yield from various fuels and to measure the rate constants pertinent to their respective thermal decompositions. There are two reaction channels of interest; those that are utilized in the fragmentation of the parent aromatic ring and those condensation routes that are used to build up high molecular weight compounds leading to soot information.

## APPROACH:

Toluene and benzene were chosen as two key aromatic compounds which are representative of the pyrolytic process. Butadiene, allene, and acetylene were selected to investigate the formation of aromatic compounds from non-cyclic species. The experimental apparatus used for the study consists of a shock tube coupled to a time-of-flight mass spectrometer. Spectra are recorded at 30 microsecond intervals for a total observation time of 0.50 - 1.20 milliseconds. Peak heights of the species of interest in the m/e range 12-300 are measured as a function of reaction time. Calibration curves are constructed which aid the conversion of peak heights to concentrations. The mixtures range from 1%-6% fuel; the balance is neon diluent.

#### STATUS:

Figures 1-3 depict the fit of a mechanism comprised of 41 reactions to the experimental data taken for a 4.3% allene - 95.7% neon mixture. The major products for allene decomposition are  $C_2H_2$ ,  $C_4H_2$ , and  $C_6H_6$ . Minor amounts of  $C_6H_2$ ,  $CH_4$ ,  $C_3H_3$ , and  $C_2H_4$  were observed. The formation of benzene was evident at 1600K, reached a maximum at 1760K, and exhibited extensive decomposition at higher temperatures. Mixtures of butadiene formed a lesser amount of benzene and mixtures of acetylene did not produce an amount of benzene that was above our threshold of detectability ( $\sim 10^{-10}$  mol  $cm^{-3}$ )

The pyrolyses of benzene and toluene were dominated by fragmentation reactions. The primary products observed were  $C_2H_2$ ,  $C_4H_2$ , and  $C_6H_2$ . There was no evidence for species formed at m/e values greater than the parent peak except for minor amounts of phenylacetylene (in the decomposition of benzene) and  $C_8H_2$  (observed in minor amounts at higher temperatures).

We have attempted to fit all of the profiles recorded in the five fuels studied using a consistent set of rate constants and thermodynamic data. We have achieved reasonable success in our modeling efforts and will discuss the difficulties we have encountered.



